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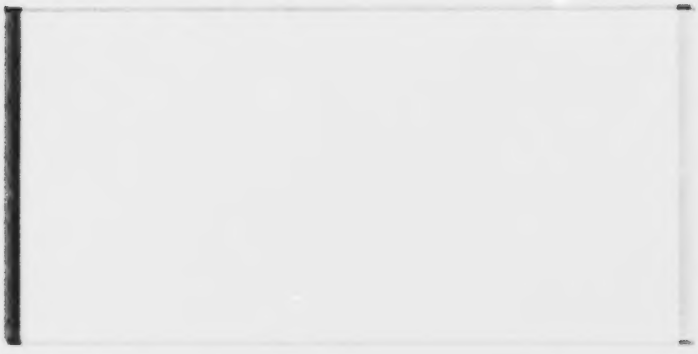

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APPLICATION OF PLASMA TECHNOLOGY TO SELECTED CHEMICAL PROCESSES

Report No 85-119-K

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ABSTRACT

The goal of this report is to select a number of conventional chemical processes well suited for incorporating plasma technology. These processes are, because of their economic importance, both compatible with Ontario Hydro overall corporate objectives and favourable to its demand management strategy.

The report reviews the fundamental aspects of plasma technology and its applications to the chemical industry. Based on economic considerations six processes have been selected. Subsequent selection criteria have ranked these processes in order of both technical feasibility for the Research Division and economic importance for the corporation and chemical industry.

The production of hydrocarbons and methanol from coal are long-range projects which ranked first and second respectively. Production of synthesis-gas from municipal refuse came third in this classification.

job	file	date	report no.
740631-540-011	836.76	February 3, 1986	85-119-K

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EXECUTIVE SUMMARY

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M. Alvarez-Cuenca
Environmental and Inorganic Research Section
Chemical Research Department

The fundamentals and potential applications of plasma technology in the chemical industry have been reviewed. Based on their social and economic impact, power demand, compatibility with plasma technology and Ontario Hydro's corporate objectives, six main chemical applications have been selected, evaluated, and ranked. This ranking, carried out by a semi-quantitative scoring method, indicates that the production of hydrocarbons and methanol from coal are the most promising areas for research and development with the greatest potential for successful implementation. The generation of synthesis-gas from municipal refuse was ranked third.

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To Mr. F.J. Kee
Director of Research

APPLICATION OF PLASMA TECHNOLOGY TO SELECTED CHEMICAL PROCESSES

1.0 INTRODUCTION

Plasma technology will be a $10.5-billion industry in the USA by 1995, rising from $359 million in 1984. The impact of this technology is to be felt in five main industrial sectors: metallurgy; synthesis of chemical feedstocks; destruction of toxic wastes; cutting, welding and surface treatments; and electronic display panels. Furthermore, the yearly rate of growth for any of these sectors will be 25% or higher/1/.

The industrial applications of plasma have reached very different degrees of development depending on the type of industry considered. In surface treatments, electronics, and metallurgy, plasma technology has reached commercial stage. However, in the synthesis of chemical feedstocks the technology is in its infancy except for the production of acetylene from coal.

A number of reports have been published in the last five years on the potential industrial applications of plasma technology/2-6/. However, the scope given in these reports places special emphasis on sectors such as: metallurgy (including strategic metals), surface treatments, and low-temperature plasma (including semiconductor technology). There is a scarcity of experimental work on the applications of plasma technology to large-volume-production chemical industries, with two well-known exceptions; acetylene production from coal (very favoured by thermodynamics) (Figure 1) and nitrogen fixation for the production of fertilizers. These two processes owe their popularity to their relative experimental simplicity. The absence of serious research efforts to incorporate plasma technology to chemical processes is even more conspicuous if one considers that in Canada the chemical industry ranks first in the amount spent on energy.

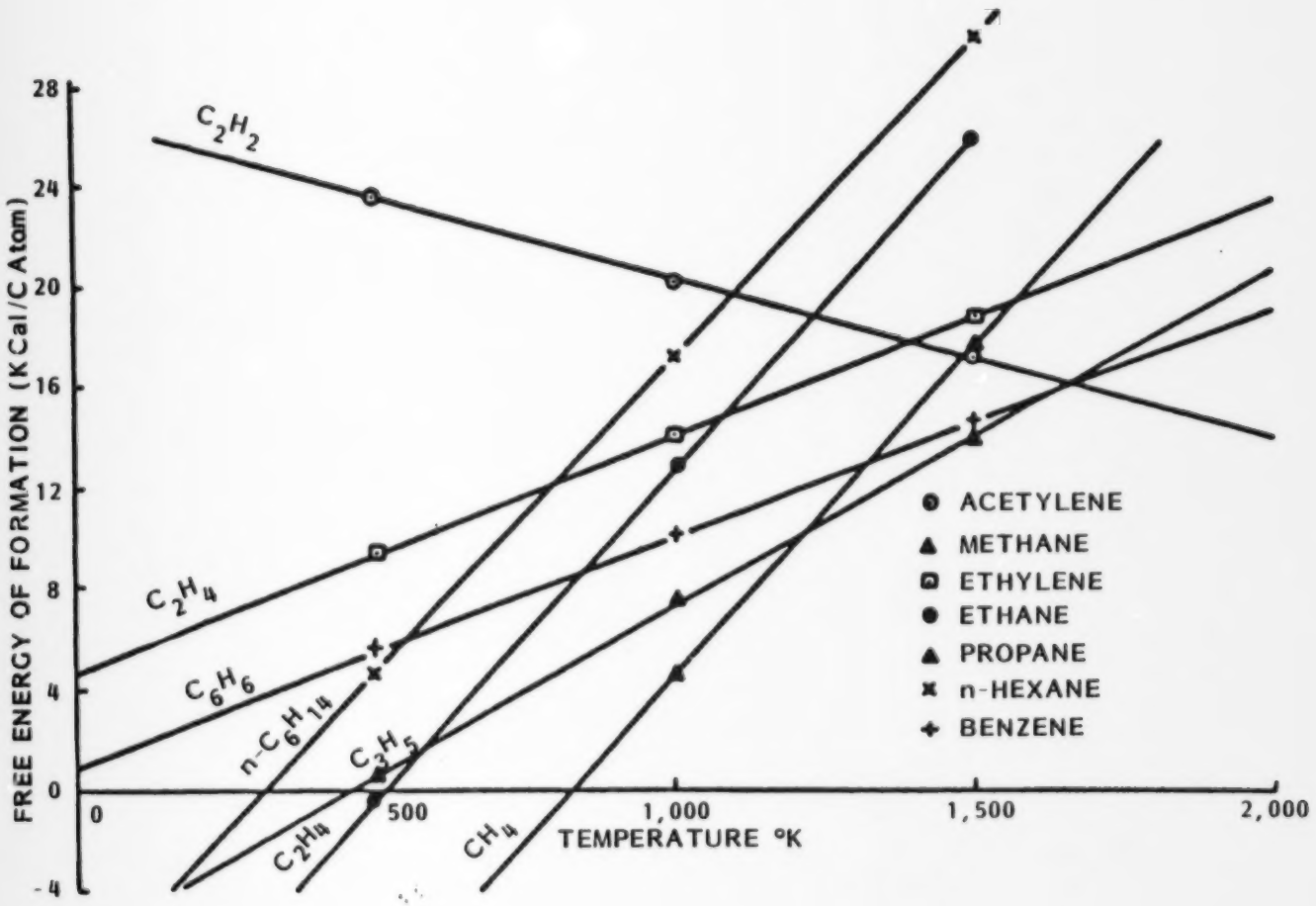


FIGURE 1

FREE ENERGY OF FORMATION OF HYDROCARBONS
AT VARIOUS TEMPERATURES /10/.

Energy is consumed in three ways in the chemical industry, namely: oil or gas as feedstocks; energy to make a desired reaction happen; and energy to separate the reaction products. The substitution of electricity for oil and gas as the driving force for plasmachemical reactions has, as will be seen, a considerable benefit for both the chemical and electric utility industries. However, a number of social, economic, and technical criteria must be met for plasmachemical technology to compete successfully with the more conventional but well established chemical processes. Based on those criteria this report will make an assessment of a number of selected chemical processes. Furthermore, the process meeting the largest number of criteria will serve as the basis for a long-range research program on plasma technology.

2.0 BRIEF REVIEW OF PLASMA FUNDAMENTALS

A plasma is defined as a quasineutral gas ionized to the extent of at least 0.1% of its molecules. As we raise the temperature of a substance, the random motion of its molecules becomes more and more violent until at last, in the region of 6000°K, the molecular bonds are broken for even the most strongly bonded material. Electrons are liberated by atom-atom collisions and the vapour becomes a mixture of radicals, electrons, atoms and molecules. Electron-electron and inelastic electron-ion collisions radiate a large amount of energy and make the gas glow with higher and higher intensity as we go up the temperature scale. A cloud of matter in such a highly excited state is known as a plasma. It is evident that the properties of such a state are very different from those of a gas - so different in fact that plasma is called the fourth state of matter. The investigation of these properties falls in the domain of plasma diagnostics and is a complex discipline by itself.

Before the most important plasma properties are stated one should explain certain concepts.

Depending on the role played by the electrons, plasmachemical processes are often divided in low-pressure plasmas ($p < 100$ torr) and high-pressure plasmas (100 torr $< p <$ 10 atm)/7/. At low pressure, the average kinetic energy of the electrons is much higher than that of the particles (radicals, molecules and atoms) and they cause the majority of the excitations, ionizations and dissociations. Thus low-pressure plasma chemistry is based on the utilization of selective reactions promoted by electrons. High-pressure plasma chemistry (thermal plasmas) which involves not only electrons but also heavier particles is characterized by the occurrence of thermal phenomena like ultra-rapid quenching and heat transfer to solids.

The electric operating conditions have an important effect on the nature of the plasma. In particular, the ratio E/p (electric field/pressure) is an indicator of the energy gain of the electrons and determines the characteristics of the discharge.

Another ratio of extraordinary importance is T_e/T_p (Temperature of the electrons/Temperature of the particles) in which T_p represents the average kinetic energy of the particles. Thus when $T_e/T_p \approx 1$, the gas temperature is high (a few thousand K) and the plasma is in thermodynamic equilibrium. These "thermal" or hot plasmas are well suited for endothermic processes. On the other hand, when $T_e/T_p \gg 1$ the gas temperature is rather low (often near ambient) and this type of plasma can be better applied in the processing of chemical specialties (low throughput and very sensitive to temperature effects). The term "high-temperature" plasma is somewhat ambiguous. For chemical engineers it implies a plasma useful for chemical processing whose temperature is below 20 000°C and which is only partially ionized (at 10 000°C 2% is ionized). Physicists, on the other hand, tend to use such a term for fusion plasmas which are fully ionized and reach temperatures $\sim 10^8$°C. This report will use the former meaning.

2.1 Thermodynamic Properties

The design of a chemical reactor requires two kinds of information:

1) What changes will take place during the process, and
2) How fast will they occur?

Thermodynamics is concerned with the first question and chemical kinetics, heat transfer, fluid flow, etc, with the second.

Thermodynamics gives two important pieces of information needed in design, (i) the heat liberated or absorbed during reaction and (ii) the maximum possible extent of reaction. The magnitude of the heat liberated or absorbed must be known for proper design. Once the heats of reaction are known, the magnitude of the heats effect during reaction can be calculated. In addition, thermodynamics allows calculation of the equilibrium constant from the standard free energies of the reacting materials. With the equilibrium constant known, the expected maximum attainable yield of the products of reaction can be estimated. In some cases, a chemical process is rapid enough so that the system is virtually at equilibrium. In those instances, kinetic information is not needed and thermodynamic information alone is sufficient.

To calculate the thermodynamic properties of plasmachemical processes, both thermal and chemical equilibria are often assumed. Also, in high-temperature plasmas one assumes that chemical kinetics are very much faster than mechanical kinetics. This hypothesis is not always valid (the residence time in the high-temperature zone is comparable to the characteristic time of reaction kinetics, ie, $\sim 10^{-6}$s). However, thermodynamic equilibrium at very high temperatures permits setting the temperature range within which a given reaction can give maximum yield. In addition, chemical equilibrium at constant temperature and pressure allows the calculation of thermodynamic and transport properties. References 8 and 9 give a comprehensive treatment of the methods used in the calculation of equilibrium diagrams.

There are a number of chemical reactions of industrial interest in which the maximum yield of a product occurs at very high temperatures. For example, in the synthesis of NO, the maximum concentration (5.2%) is attained at 3500°K/7/. However, NO decomposes during slow cooling. It is here where a fast quench of the reaction products prevents reversible reactions and yields maximum concentration of the desired product. Thus, freezing of the reaction constitutes a critical step in the selection and yield of the products.

A unique feature of plasma processes is their high enthalpy recovery. The enthalpy of a combustion flame, as opposed to that of a plasma, is determined by the nature of the reactants and the combustion temperature, and is relatively small, for example an Eastern US sub-bituminous coal could deliver 32.5×10^3 kJ/kg. On the other hand, in a plasma, energy is supplied by both an external source and by the gas flow, and energies as high as 10^8 kJ/kg can be attained. G. Fey of Westinghouse has reported/12/ recovery energies exceeding 70% of the disposable enthalpy of plasma heaters as opposed to 10% of the disposable enthalpy for an air-natural gas heater (Figure 2).

Because of the crucial importance of thermodynamics in the development of both realistic research programs and plasma reactors, a thermodynamic analysis of any chemical process under consideration must be carried out.

2.2 Plasma Generators

Plasma generators have, according to their specific applications, a large variety of design configurations, and as expected from a young technology, many of these reactors require frequent modifications. Nevertheless, plasma generators can be classified as follows:

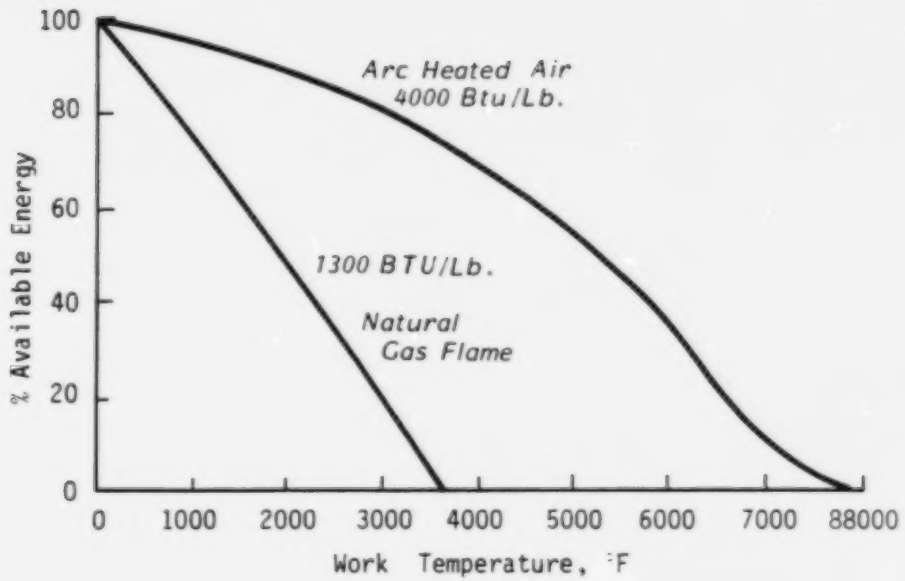


FIGURE 2
EFFICIENCIES FOR HIGH TEMPERATURE HEATING [12]

1) by the type of current
2) by the plasma generating method
3) by the position of the anode with respect to the plasma arc
4) by the arc stabilization method, etc.

A detailed description of known plasma generators is beyond the scope of this report. Furthermore, a number of recent publications have given considerable importance to this subject/4,7,13-15/. However, a brief description of some of the plasma generators will help in understanding the choice of a reactor for a given industrial application.

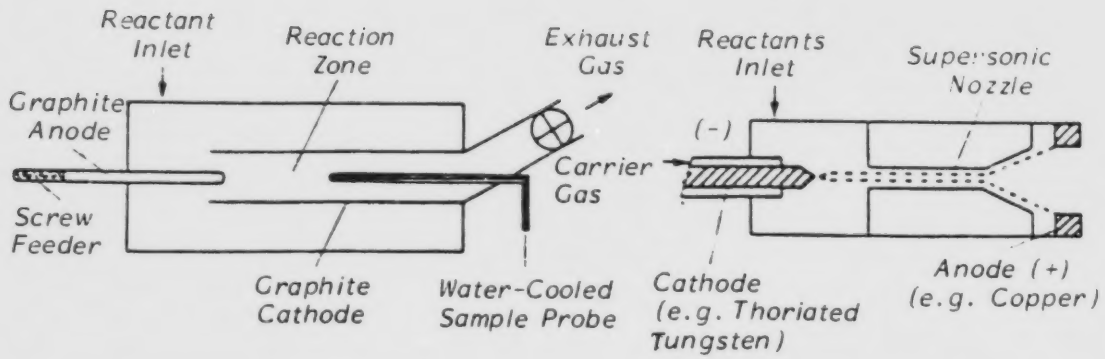
2.2.1 dc Generators

The principal types of dc discharges are the dark or Townsend discharge, the glow and the arc discharges. Since only the glow and arc discharges are of interest for carrying out chemical reactions only these two types will be discussed.

In a glow discharge the cathode emits electrons under the bombardment of fast ions. The thermal effects which are negligible are not necessary for sustaining the discharge.

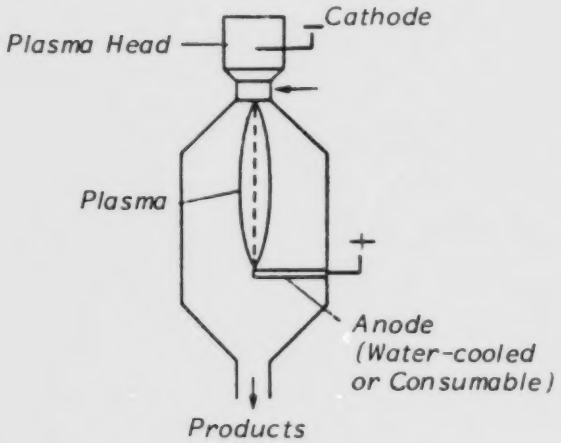
Chemical reactions occur predominantly in the region of the cathode fall (voltage drop within a given distance of the cathode) and in the positive column (zone between the anode fall and cathode fall). The highest rate of reaction per unit volume is observed in the cathode-fall region because the field intensity and hence the number of high-energy electrons is larger. However, the cathode-fall region is small compared to the total reaction zone (distance between the electrodes) and, in fact, the reaction rate is controlled by the positive column. Glow discharge operates under a variety of conditions, the most familiar application being in lighting; neon, sodium mercury lamps, etc, and under special conditions of high voltage and low pressure, can be applied in crystal growing, melting, and chemical processing.

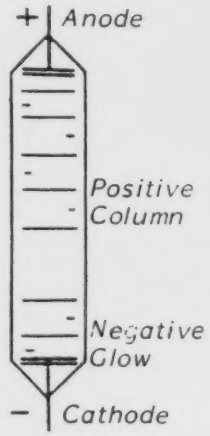
The arc discharge as opposed to the glow discharge depends mainly on the thermoionic emission of electrons from the cathode to sustain itself. The discharge region can be divided into three zones but the sum of the cathode and anode falls is very small. The current density in the arc is much greater than in the glow discharge and so is the power density despite the lower voltages. This type of generator is likely the most widely used and the most stable (Figure 3A to C). It, often, consists of a tungsten cathode in the form of a cylindrical bar and a concentric pipe anode made of copper. The gas plasmagene (carrier or



A. High Intensity Arc Reactor (e.g. C_2H_2

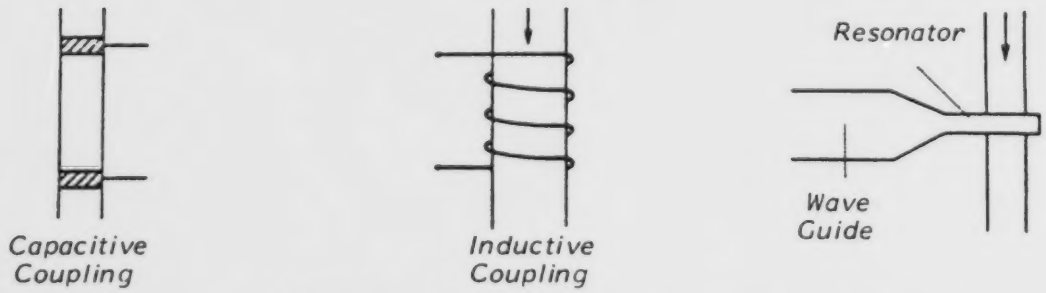
B. Constricted Arc Plasma Jet





C. Transferred-arc Plasma Jet (e.g. Hydrocarbon Reforming - Thermal Dynamics Corp.)

D. Glow Discharge Reactor (e.g. NH_3 Synthesis)



E. Radio Frequency Discharge (e.g. NO Synthesis

F. Microwave Discharge (e.g. SO_2 Oxidation)

FIGURE 3

PLASMA REACTORS
D.C GENERATORS (A,B,C,D) H.F. GENERATORS (E,F) /16/

at times reactant gas) flows past the arc which is confined in a nozzle, or cylindrical anode, between the two electrodes (Figure 3B). For some metallurgical applications energy is better transferred with the arc struck between the cathode and the anode (Figure 3C).

Arc plasma generators are very efficient in converting electric energy into kinetic and chemical energy. Indeed, efficiencies above 70% have been claimed by many manufacturers. This efficiency is a function of the input power and Estey and Connolly/17/ have expressed it as:

$$\eta = C\ (1 - e^{-KP}) \qquad (1)$$

where C and K are constants dependent on the generator design, and P is the input power (in kW) to the plasma generator.

The dc arc plasmajet is a versatile tool capable of temperatures up to 50 000°K and velocities in the subsonic to the Mach 20 range. Power inputs vary from less than 1 kW to several MW (Figure 3B and Table I).

Plasma jets are used as heat sources for processes such as welding, cutting, spheroidizing and spraying and to carry out chemical reactions at high temperatures. In plasma chemical processes, fast heating of the reactants and fast quenching of the products are of fundamental importance.

2.2.2 High-Frequency Generators

Radio-frequency and microwave-sustained discharges are of special interest in studies of electrically induced chemical processes since the presence of the electrodes in the discharge zone may be eliminated. Figure 3 shows some of the methods to generate plasma from high-frequency power.

In a high-frequency discharge, energy is transferred from the electric field by electrons produced during the ionization of gas atoms or molecules. These electrons gain energy from the field and collide elastically with gas molecules. The average power transferred per unit volume of gas through this mechanism is

$$\bar{p} = \frac{ne^2E_o^2}{2m} \frac{\nu_c}{\nu_c + \omega^2} \qquad (2)$$

TABLE 1

MAIN CHARACTERISTICS OF PLASMA SOURCES/13/

Type of Plasma	Maximum Power (kW)	Frequency Range (kHz)	Pressure Range (Torr)	Arc Current Intensity (A)	T_e/T_h	T_h (K)	Thermal Efficiency %	Nature of the Products Treated	Quantity of the Products Treated (g/s)
Glow Discharges	10	0	10-100	10^{-2} - 1	5-100	< 1000		Non agressive gas	10^{-3}
Corona Discharge	5	< 500	760	$< 10^{-1}$	5-100	300		Any gas	< 1
Microwaves (MW)	5	310^5 - 210^6	10-760		2-100	< 3000	20	Any gas	$< 10^{-1}$
HF	1000	10^3 - 2.10^4	10-760		1-50	<10000	< 50	Any gas or solid particles	<50
Arcs	10000	DC or 0.1	100-760	>50	1-5	2000 20000	< 90	Non agressive gas solid particles	<100

where E_o is the amplitude of the high-frequency field, m and n the mass and electron density respectively, ν_c the elastic collision frequency and ω the applied field frequency. In general, ν_c lies between 10^9 and 10^{11} collisions/s and $\omega \approx 10^7$ Hz which implies that for radio-frequencies where $\nu_c \gg \omega$ the effect of ω is negligible.

Low-frequency plasma generators have an anode-cathode configuration different from dc generators due to the alternating function of the two electrodes which in this case are cooled copper cylinders. A high-frequency voltage is sometimes superimposed at the arc to prevent its extinction when the current goes through zero. A number of different electrode configurations and ac generators have been designed in Europe/7/.

The main advantage of the high-frequency plasma generators is the separation of the plasma from the electrodes. Since there is no risk of plasma contamination with the electrodes, reactive gases such as chlorine and oxygen can be satisfactorily processed. Within high-frequency plasma generators the type most used is the induction-coupled generator which can attain a power of 1 MW and an efficiency of 50% (Figure 3E). The induction coil is around a quartz tube which encloses the plasma where temperatures of up to 10 000°K can be achieved. A water jacket controls the temperatures at the wall of the tube. The energy transformation of an HF generator depends on both the type of gas, its pressure and the operating frequency. High frequency torches are used in very specific applications such as chemical processes involving very reactive gases, growth of crystals, etc. A summary of the characteristics of plasma generators is given in/7/.

2.2.3 Plasma Reactors

Because of the complexity of plasma reactions, predictability and hence systematic design of plasma reactors is difficult. Nevertheless, for a given chemical process the plasma reactor design should optimize energy yield, conversion, and product selectivity. In turn, these factors depend on the temperature and pressure in the reactor, residence time of the reactants, mixing between plasma and reactants, and products quenching rate. Indeed, at low field strength and pressures the degree of primary ionization in the discharge is dependent on the electron energy Q and collision frequency of the electrons, both of which are proportional to the reduced field E/P. Here E is the electric field and P the pressure. Since molecular ionization increases with current density J the energy yield Y can be expressed as:

$$Y = \psi \left(\frac{E}{P} J\right) \qquad (4)$$

In some cases the energy yield will not increase with J inasmuch as kinetics may favour product dissociation more than product formation. Also, yield will be dependent on residence time, for example for a plug flow reactor

$$\tau = \int_{o}^{x} \frac{d_x}{V_f r} \qquad (5)$$

where V_f is molar volume, r is the reaction rate and x is the conversion. Thus, the energy yield has the form:

$$Y = \phi\left(\tau, \frac{E \cdot J}{P}\right) = \phi\left(\tau, \frac{\Pi}{P}\right) \qquad (6)$$

and conversion will be a function of the same variables. Eremin/18/ has shown that in a given reaction there is a critical value of x for which Y is optimum.

A way of improving energy yield is to minimize decomposition of the product as it is formed. This also contributes to selectivity since many consecutive, parallel and reversible reactions occur. Thus, minimizing residence time keeps product concentration low. Similarly an increase in power density Π will increase decomposition as it happens with the increase in carbon formation from hydrocarbons.

Design features such as quick removal of products, selectivity and quenching are interrelated. These factors are controlled as follows:

1) Selective removal by absorption in a liquid phase or by chemical reaction thus giving rise to a more stable product.

2) Residence time, by operating under plug flow. However, good mixing should be promoted before the reactor. Good mixing is extremely important and it is quite difficult to obtain between a cold low velocity reagent feed and a high temperature, high velocity plasma stream. The problem might become more acute on the laboratory scale because the plasma jet is itself in the laminar flow regime, mainly due to the high gas viscosities at this temperature/19,20/. Scale-up of these reactors should improve mixing since the Reynolds numbers will be higher.

3) Type of discharge, for example the discharge could be pulsed so that there is enough activation for product formation but minimum activation for product decomposition.

4) Adsorption in fluidized or suspended phase to increase selectivity or quenching. In the latter case there are a number of methods such as: a) direct spraying with a cold inert fluid (water, liquid nitrogen, etc) which gives quenching rates up to 100°K/μs; b) heat transfer to a cold surface with average quenching rates of 1°K/μs; c) adiabatic expansion of gases up to 1°K/μs; d) passage through a fluidized bed, up to 100°K/μs; and e) expansion through a supersonic nozzle which can give quenching rates of the order of 100°K/μs.

The quenching system is often a reactor itself since by its action the equilibrium composition is frozen or the recombination reactions which yields the desired products are favoured. Figure 4 depicts the role played by quencher in the generalized diagram representing a plasma process.

For a plasmachemical reactor to be successful the following criteria must be met:

1) Continuous operation capability
2) Operational flexibility and
3) High electrical efficiency

The last criterion is calculated by the following energy balance. The arc voltage and current may be measured and their product (neglecting power supply ripple) yields the total input. Deducting from this the heat losses to the electrode cooling water (determined from the temperature rise of a known flow of coolant) and assuming the wall losses are negligible, the net power input to the arc gas may be determined. The ratio of the net power input and the mass flow rate of the gas (plasmagene and reactant), gives the average enthalpy, ie, units of energy per unit mass. Finally, the operating electrical efficiency is obtained as the ratio of the power input to the plasma to the total power input to the generator.

In general, it can be stated that plasma reactors (high-intensity arc, plasma jet and radio-frequency reactors) are increasingly used in chemical processes - particularly in endothermic ones. The "cold" plasma reactors using glow and microwave discharges have a distinctive role to be played in industries demanding less severe operating conditions (electronics, surface treatments, etc). Electricity is one of the most important cost factors; therefore the commercial

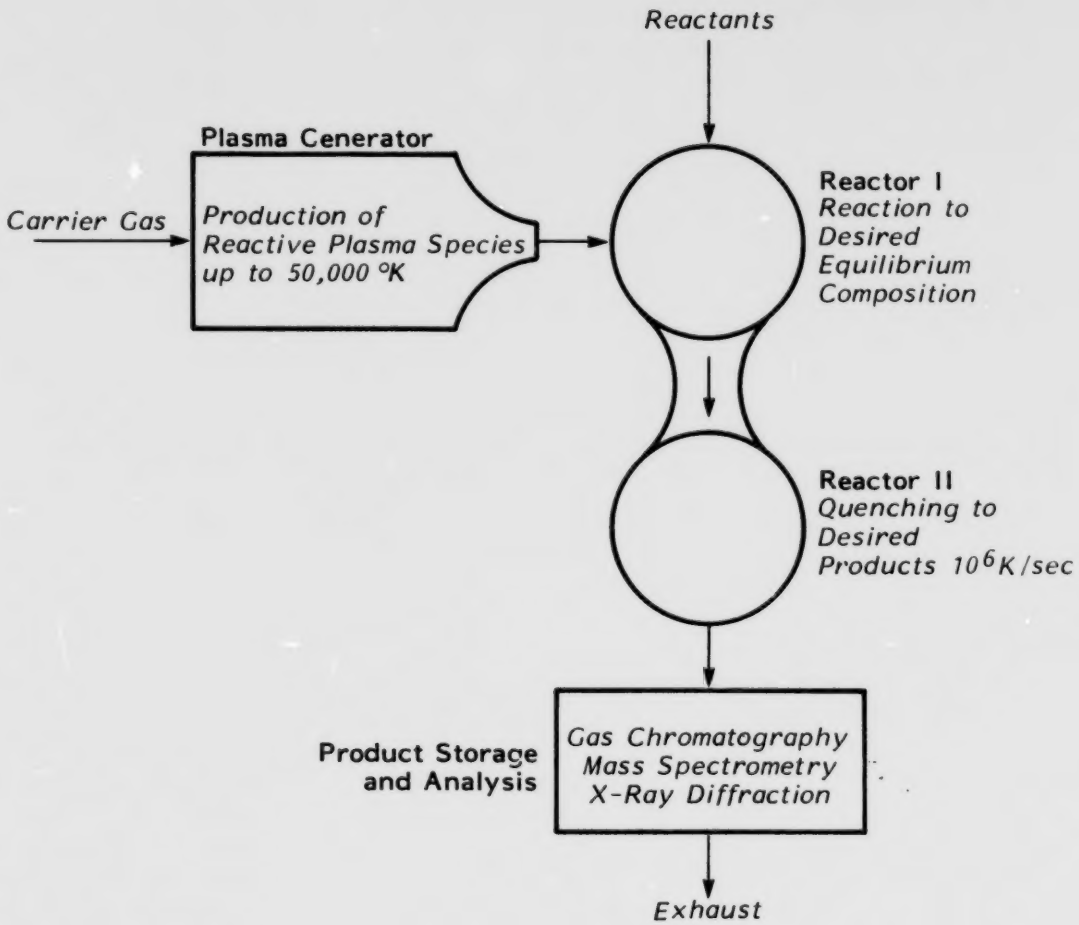


FIGURE 4

DIAGRAM OF PLASMACHEMICAL PROCESS/14/

viability of a process will heavily depend on its electrical efficiency and hence on the reactor design.

3.0 APPLICATIONS TO THE CHEMICAL INDUSTRY

The industrial use of plasma has been frequently based on two arguments, namely the low cost of electricity from nuclear plants and the fast decrease of the world reserves of oil and natural gas. In reality, neither the oil nor the natural gas have reached the astronomical prices predicted in the early 70's. In addition, the generation of electricity from nuclear plants has not produced the "widespread availability of cheap (virtually free!) electrical energy" predicted by some in the 60's/2,6,22/. Evidently, the present oil glut is a transient phenomenon and, eventually, liquid fuels and petrochemical feedstocks will be in short supply. Unfortunately, these factors contribute to the inertia to modify the current conventional industrial processes.

A considerable amount of research on high-temperature chemical processes has been carried out. However, for reasons to be explained in the next section, few are immediately amenable to industrial exploitation. These processes include one or more of the following reactions:

1) Endothermic reactions in which the free energy decreases with increasing temperature and the products are stable at high temperature. An example of this is the production of acetylene from coal.

2) Reactions having favourable thermodynamics at low temperatures, but where the kinetics require a high temperature for a finite reaction rate. The syntheses of boron nitride or titanium nitride are prime examples of them.

3) Reactions involving intermediates that do not exist at ordinary temperatures. These processes offer many interesting possibilities and research in this area is virtually untapped since plasma plays the role of a catalyst. Many chemical specialties could be obtained by these types of reactions.

4) Reactions in which the properties of the product are enhanced by exposure to high temperatures. This property could have an extraordinary importance in the manufacture of catalysts. Certain metallic oxides treated with high temperature plasmas have revealed surface areas much greater than those produced with conventional methods.

In general, the industrial use of plasma has far more advantages than disadvantages. In fact, as shown in Table II, most of its disadvantages are inherent to its condition of young technology. There is little doubt that as new diagnostic methods and materials are developed, and more technical data are collected, plasma technology will be economically more acceptable.

In the meantime, research on plasma technology should be seen not as another production process subject to the same return on investment calculations, supply and demand laws, etc, nor as an endeavour justified in itself. The aim of this report is the selection of a number of chemical processes of industrial interest. This selection will be based on a synthesis of both their socioeconomic impact and their experimental feasibility.

4.0 CRITERIA FOR THE SELECTION OF PLASMACHEMICAL PROCESSES

Canada has one of the largest chemical industries in the world. The Canadian output per person in chemical process industries such as, benzene, toluene, xylene, ethylene, ammonia, urea, chlorine, sulfuric acid and phosphoric acid, ranks among the three largest in the world. In 1981, the shipments of the three classes of industrial chemicals (petrochemicals, inorganic chemicals, and organic and specialty chemicals) were valued at about $8.2 billion if fertilizers are included. The chemical industry in Canada ranks fifth in value of shipments (Figure 5) and is second only to pulp and paper in its added value (Figure 6). Already the chemical industry earns more from export than does the primary iron and steel industry and it could surpass the pulp and paper industry in the near future. Another datum of extreme importance in the assessment of our research program is the demand by the chemical industry for electric energy. For example, the inorganic chemical industry, one of the largest users of electricity in the country, purchased $138 million worth of power in 1981. In addition, the fertilizers, organic, inorganic and petrochemical industries combined, spent $672 million in utilities (Figure 7). Thus, the chemical industry is, because of its economic importance, its consumption of electricity, and large added value, a prime target for plasma technology. Indeed, the lack of full fledged commercial processes, as opposed to the metallurgical industry, is partly due to the considerable complexity of the plasma chemical reactions.

4.1 Preliminary Selection

R&D project evaluation and selection has a high inherent uncertainty, noneconomic criteria, and time-dependent data and decision making considerations. In this report, the selection

TABLE II

EVALUATION OF PLASMA PROCESSES RELATIVE TO CONVENTIONAL ONES

Advantages	Disadvantages
• Exceptionally reactive medium	• Lack of diagnostic tools for industrial processes.
• Higher power density	• Very large scale-up factor, therefore uncertainty in design.
• Higher available energy and heat transfer efficiency.	• Higher requirements from the materials of construction.
• Faster start-ups and shut-downs.	• Need for reliable quenching to prevent recombination.
• Much higher operating temperatures can promote kinetics and thermodynamics of desirable reactions	• Lack of reliable data and other problems associated with young technologies.
• Offer strong incentives to simplify flow-sheets of conventional processes.	• Expensive instrumentation and control equipment.
• Compatibility with almost any gas (inert, oxidizing, reducing, etc) giving rise to a wider range of chemical processes.	
• Environmentally more acceptable since it is both a closed system and the volume of gases generated is much smaller (combustion is not the temperature promoting agent).	

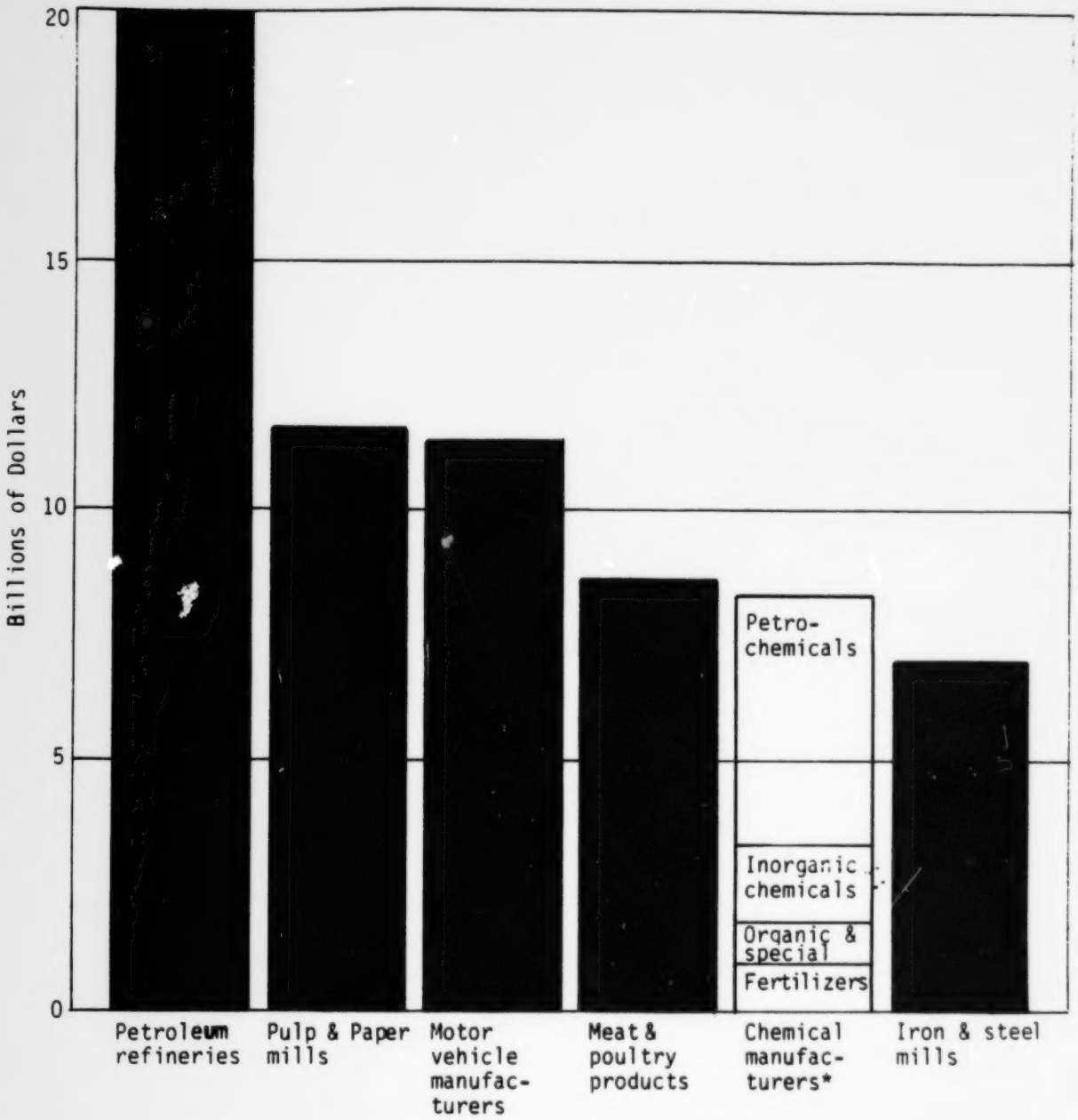
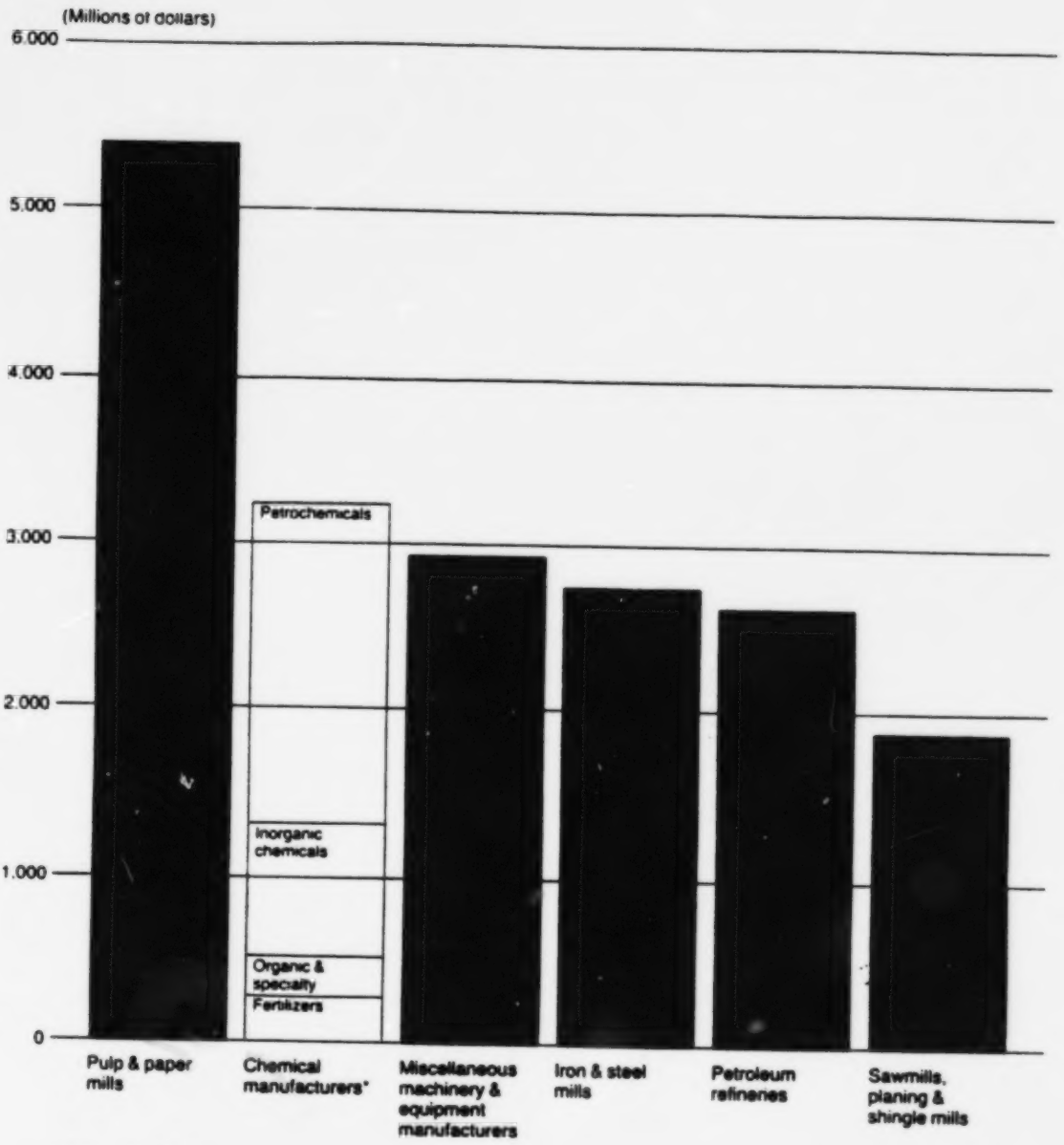


FIGURE 5

CANADA'S TOP SIX MANUFACTURING INDUSTRIES, 1981 /24/
VALUE OF SHIPMENT

168074-RD



*Based on CCPA data.
Source: Statistics Canada except where noted.

FIGURE 6
VALUES ADDED BY LEADING CANADIAN MANUFACTURING INDUSTRIES
1981/24

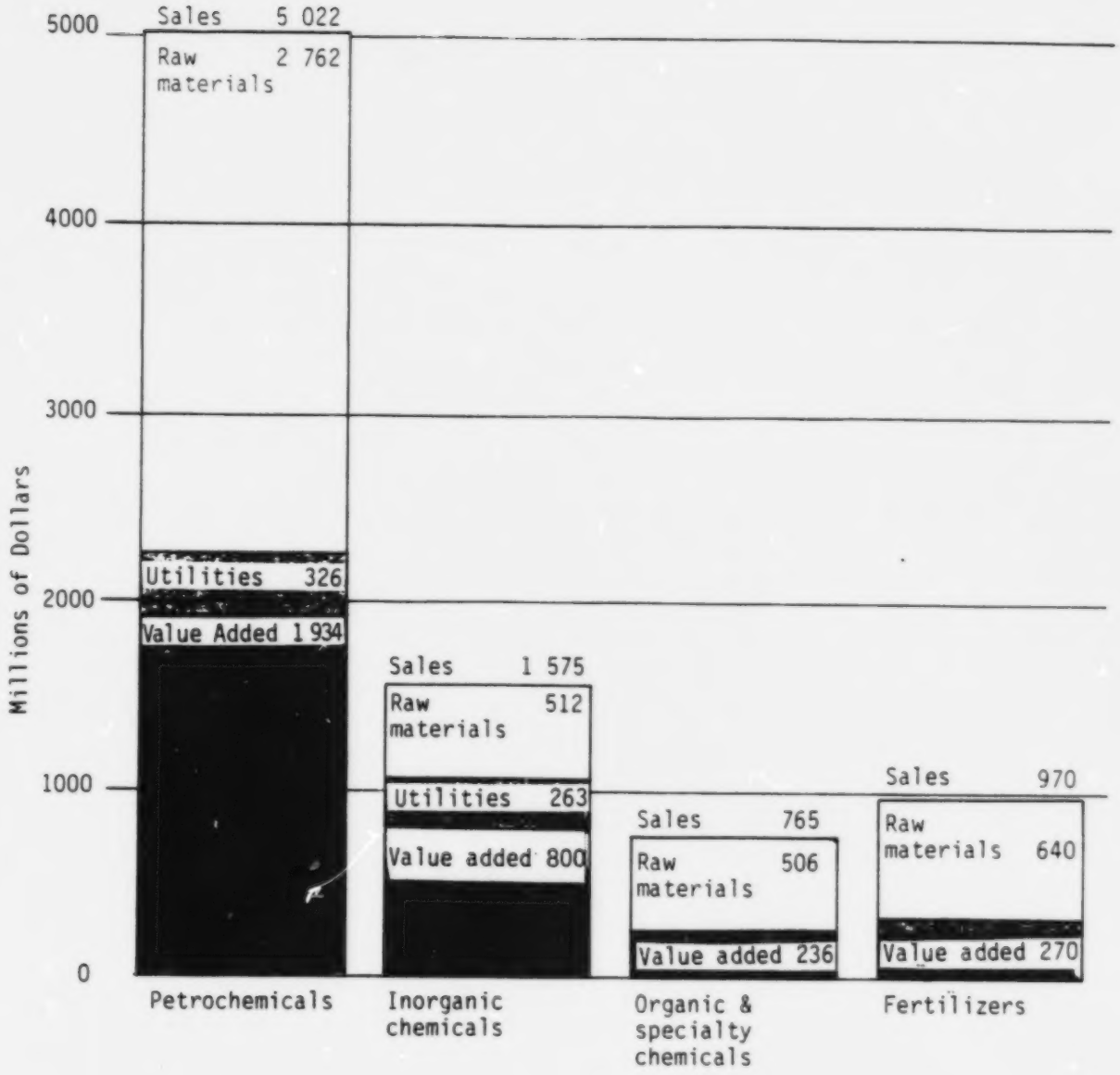


FIGURE 7

CHEMICAL MANUFACTURING INDUSTRY, 1982 /24/
SALES BREAKDOWN SHOWING VALUES ADDED

168078-RD

of six preliminary processes has been on the study of conventional processes in the chemical industry, their social impact, electric power demand, and susceptibility to plasma technology applications. These projects are:

1) Petrochemical feedstocks from coal
2) Synthesis-gas and methanol from coal
3) Nitrogen fixation
4) Synthesis-gas from municipal refuse
5) Phosphorus and phosphoric acid production
6) Cement production

They are deliberately wide in scope to allow for further selection once the experimental conditions of the chosen project are established. A brief description of them is given in the next section. In addition, they will be classified according to a scoring method/26,27/ presented in Appendix I.

5.0 DESCRIPTION OF SELECTED PROCESSES

5.1 Hydrocarbons From Coal

Energy markets and the oil market in particular are likely to remain fictitiously stable through the mid-1980s but highly uncertain, or even increasingly tight thereafter. Indeed, if the roduction of crude oil outside the Middle East continues at levels approaching the maximum, the dependence of the industrialized countries on Middle East Oil could reach politically dangerous levels by the mid-1990s/65/. Thus, although the short-term outlook for oil indicates relatively stable prices and ready availability, the strategic reasons for continuing with programs to develop new technologies to produce petrochemicals and liquid fuels from coal remain. For example, the USA spent $90 million in 1980 in foreign oil - more than $10 million an hour. To these economic considerations, one has to add the strategic need for a constant and reliable supply of oil.

Among the technologies for the production of liquid fuels on a large scale, coal liquefaction is the most important option. The technical feasibility of producing oil and other petrochemicals from coal goes back to the 19th century. However, the advent of plentiful oil supplies, low-cost natural gas and advanced technology made the use of coal by the chemical industry decline drastically. In recent years coal liquefaction processes have been demonstrated in countries such as South Africa, USA and Germany. South Africa, in particular, is the only country to date to have developed a fuel and petrochemical industry based on coal. However, the technology to produce a full line of chemicals such as ethylene, polyolefins and aromatics, needs considerable development before

commercialization/31,32,33/. Small process development units are in operation in conjunction with pilot plants in the above countries and Japan. Also, a full-scale methanol-to-gasoline (MTG) plant (13 000 barrels/day), developed by Mobil, is in operation in New Zealand. Literature on conventional processes to produce fuels or chemical feedstocks from coal is extraordinarily abundant. Indeed, a detailed description of these processes would go beyond the boundaries of this report. A report covering the most advanced coal liquefaction is being completed.

The production of petrochemicals and liquid hydrocarbons, mainly acetylene, using plasma reactors experimentally began in the 1950s.

High speed pyrolysis of coal in a plasma reactor was considered already in the 60's as a source of "... a very different spectrum of products..."/21/.

Amman et al/34/ processed coal for the production of light hydrocarbons in a special dc arc reactor. A high fraction of the coal was converted to useful products. Preliminary analyses showed 10% CH_4, 5% acetylene and 72% hydrogen.

Patrick and Gannon/35/ of AVCO have developed a process which can economically compete with oil-based processes. Apart from acetylene, considerable amounts of C_2 and C_3 olefines were obtained. A rotating dc arc reactor and particularly a suitable propane quench contributed to the presence of important quantities of ethylene.

An indicator of the development of these processes is the insignificant effort devoted to the production of some of the most important petrochemicals: Benzene, toluene, and xylene (BTX). Only one paper/36/ by Szymansky et al has reported the presence of benzene from the pyrolysis of brown coal in a plasma reactor. This lack of work in this area is more conspicuous if one considers the weight that BTX have in the petrochemical industry (Figure 8 and Table III). Either as liquid fuels and octane boosters or as basic chemical feedstocks, BTX play a central role in the Canadian economy.

The production of liquid fuels from coal was, among the areas evaluated to select a long-range research program, the first choice. This selection was based on the semiquantitative method used in Operations Research called the Scoring Method. The score for the selection of the program was based in the algorithm presented in Appendix I, Section 6. To quantify the weight of the criteria adopted for each of the programs, a

number of prestigious researchers in the Chemical Process Industries were consulted and their views incorporated in the Scoring Method. Appendix I describes the technique in more detail. Table IV shows the scoring values. The large sales volume that the petrochemical industry has and the high potential for research joint ventures makes this program especially attractive. The expertise and experimental capabilities existing in Ontario Hydro for this type of program was also an important factor in the resulting high score.

5.2 Methanol Via Synthesis-Gas from Coal

Two high-powered executives from the car industry, D.E. Petersen (President of Ford Motor Co) and U. Seiffert (Executive Director of Volkswagenwerk A.G.) recently gave similar messages at the Sixth International Symposium on Alcohol Fuels in Ottawa. After outlining Ford's extensive experience in testing various alternate fuels, D.E. Petersen said, "We have looked at methanol as the most likely of the possible large-scale replacements for petroleum-based gasoline in North America". Seiffert, based on an equally impressive record of Volkswagen, concluded that, "...among all alternative fuels, methanol still has the highest potential for worldwide use"/37/. In reality, methanol is the first organic chemical with a production of 1670 thousand of metric tons in 1983 (Table III). Only the fact that oil supplies are, currently, stable and inexpensive has, to a certain extent, reduced the momentum to further use it as an octane booster. Ontario Research Foundation under contract to Celanese Canada Inc has recently completed a two-year evaluation of a methanol/gasoline blend for unmodified car engines. The tests showed that a blend constituted by 4.75% methanol, 4.75% cosolvent, 90.5% gasoline "...performed just as well as unleaded gasoline in all respects"/38/. Thus, the view held by the car manufacturers is that the development of methanol as an automotive fuel is only waiting Government aid in the form of subsidies or helpful policies.

Methanol from coal is, in terms of energy efficiency, almost comparable to methanol from natural gas (Figure 9). A vast pool of literature on the production of methanol from coal exists. However, information on the production of methanol by plasmachemical processes is rather meagre in the open literature/39,40/.

Stuart et al/40/ have gasified finely divided peat using a steam plasma in a co-current downward transport reactor. A ratio of H/CO of 1.8 was achieved and a maximum carbon conversion of 89%. Reaction models developed by those workers show that both a 90% conversion and a H/CO of 2 can be achieved, thus making the process commercially usable. Conversion to methanol and

TABLE III

CANADIAN PRODUCTION OF SELECTED CHEMICALS

Thousands of metric tons	1983	1982	1981	Change 1982-83
ORGANIC CHEMICALS				
Benzene	580	519	571	12%
Butadiene	133	118	126	13
Butylene	138	107	124	29
Ethylene	1196	1013	1330	18
Formaldehyde	90	70	85	29
Methanol	1670	na	na	--
Propanol	63	67	73	-6
Propylene	715	693	671	3
Toluene	411	471	480	-13
Urea	1445	1231	1303	17
Xylene	432	431	409	0
INORGANIC CHEMICALS				
Ammonia, anhydrous 100%	2888	2509	2654	15
Ammonium nitrate	934	1018	1212	-8
Ammonium phosphate	1259	1027	1355	23
Chlorine	1385	1233	1292	12
Hydrochloric acid	170	143	186	19
Nitric acid	855	977	1158	-12
Phosphoric acid, 100% P_2O_5	656	553	744	19
Sodium chlorate	294	264	255	11
Sodium hydroxide	1528	1367	1458	12
Sulfuric acid	3686	3131	4117	18
SYNTHETIC RESINS				
Polyesters, unsaturated	26	27	26	-4
Polyethylene, high density	211	194	222	9
Polyethylene, low density	412	376	410	10
Polyvinyl chloride	243	193	222	26

na = not available. Source: Statistics Canada

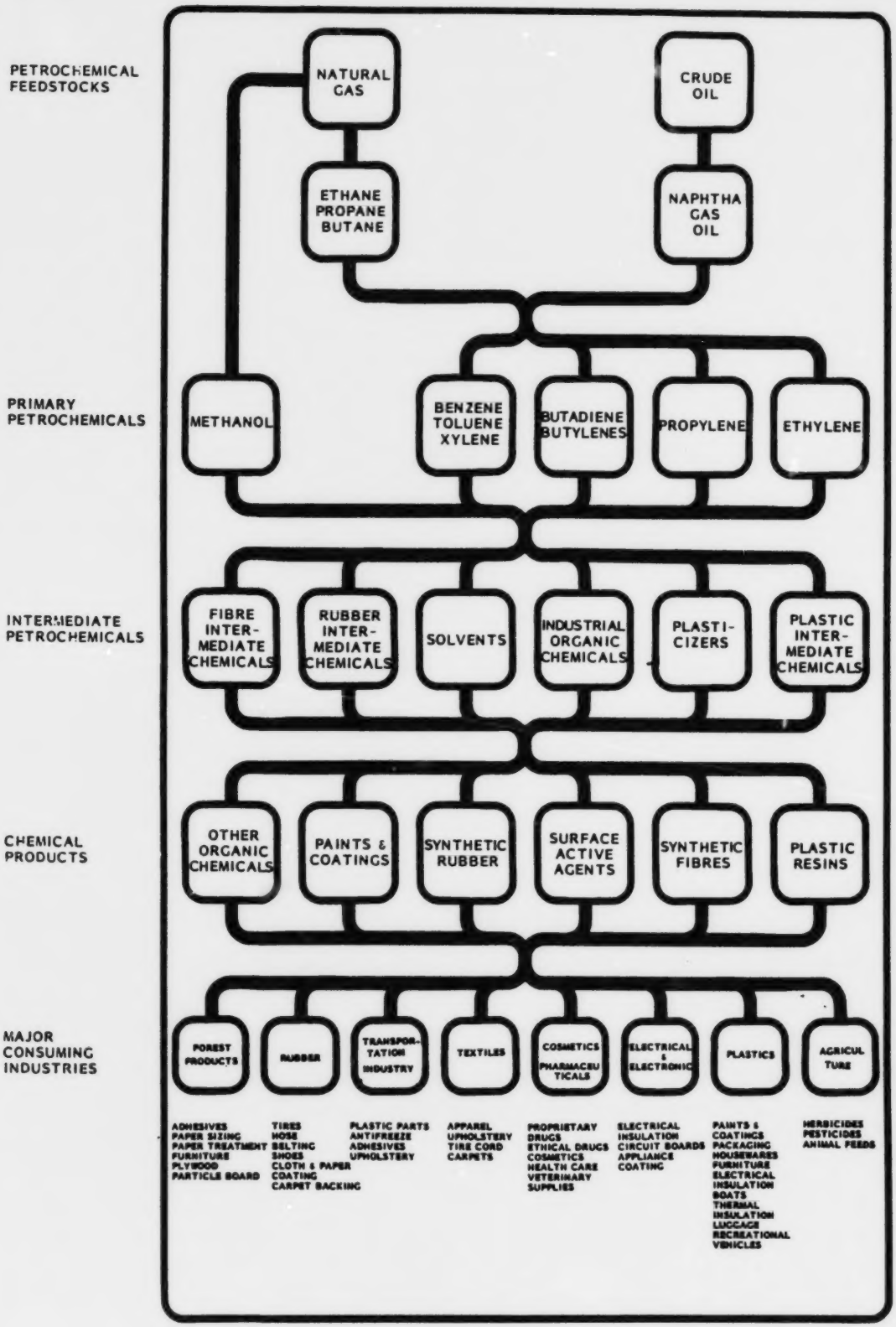


FIGURE 8

DIAGRAM OF THE PETROCHEMICAL INDUSTRIES/24/

methanol derived products is to be achieved in a subsequent step in which water will be fed to the plasma reactor. Technoeconomic studies indicate that the process is very promising/41/.

As shown in Table IV this project had the highest scoring after the production of basic petrochemical feedstocks from coal. The experimental feasibility is comparable to the aforementioned project. However, the sales volume potential for joint research ventures and added value ratio were considerably lower.

5.3 Nitrogen Fixation

The direct fixation of nitrogen has an extraordinary economic importance as shown by the production volumes of NH_3 and HNO_3 (Table III). As with the two previous processes, nitrogen fixation is a well established technology. Thus, productivity improvements will come either from the introduction of new catalysts or better energy management. In any event, the profit margins are already small so that any important increase in productivity is bound to come through a drastic departure from the conventional technology now in place. The fixation of nitrogen in a plasma reactor might be the sought technology.

Nitrogen fixation using plasma chemistry has been the subject of detailed investigation because among other interesting features it is very well suited to high-temperature processing.

The production of NO, HNO_3, NH_3, HCN, CN_2, etc has been abundantly reported/2,3,16,13-15,17,21,41,43/. When air is heated in a plasma arc to temperatures in excess of 3000°C, the mixture will contain 6% volume of NO. Subsequent air quenching of NO produces nitrogen dioxide which absorbed in water yields nitric and nitrous acids. That is:

$$N_2 + O_2 \rightarrow NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

The strong demand for fertilizers at the beginning of this century prompted the rapid development of the arc process until the appearance of the Haber-Bosch process for ammonia in the early 20's.

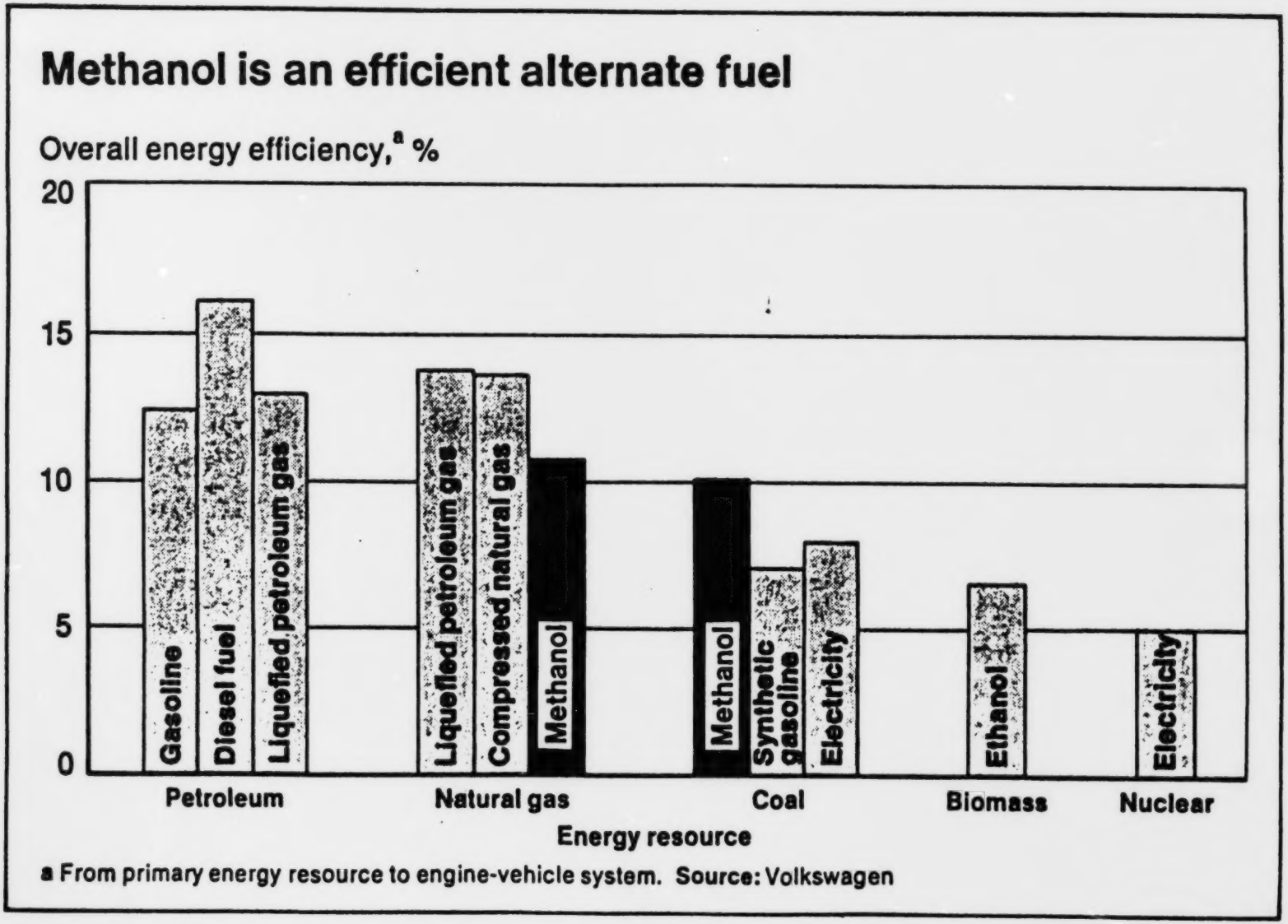

Methanol is an efficient alternate fuel
Overall energy efficiency,[a] %
20
15
10
5
0
Gasoline
Diesel fuel
Liquefied petroleum gas
Liquefied petroleum gas
Compressed natural gas
Methanol
Methanol
Synthetic gasoline
Electricity
Ethanol
Electricity
Petroleum
Natural gas
Coal
Biomass
Nuclear
Energy resource
a From primary energy resource to engine-vehicle system. Source: Volkswagen

FIGURE 9./37/

TABLE IV

Selective Indicators for the Evaluation of a Plasma Research Project

Process	Sales Volume (Billions of Dollars)	Ratio* $\frac{AV}{RM + U}$	Raw Materials and Cost**	Potential to Simplify Conventional Process	OH Expertise and Experimental Feasibility	Cooperative Projects Potential	Selective Score
Criterion Weight	0.7	0.7	0.4	0.6	0.8	0.6	
Basic Petrochemical Feedstocks from Coal	5.00 (1983)	~0.62	Low grade coals, H_2 Moderate (4)	Very high (8)	Very high (8)	Very high (8)	183
Methanol from Coal	1.67 (1983)	~0.44	Low grade coals, steam Moderate (4)	Very high (8)	Very high (8)	Moderate (4)	134
Nitrogen Fixation (NO, NH_3) Fertilizers	2.90 (1984)	~0.38	Air, H_2 Natural Gas High (6)	High (6)	High (6)	Moderate (4)	106
Gas Synthesis from Municipal Refuse	0.76 (estimated 1983)	~1 (assumed)	Refuse Low (2)	Very high (8)	Low(2)	Very high(8)	116
Phosphorus and H_3PO_4	0.65 (1983)	~0.38	Phosphate rock, carbon, silica Low (3)	Moderate (4)	Low (2)	Low (2)	47
Cement Production	~0.78 (1983)	~1.03	Cement rock Limitestone, Clay, coal Gypsum, Sand Moderate (4)	High (6)	Low (2)	Low (2)	36

*AV = added value, RM = raw materials cost, U = utilities

**Scoring Scale: 0 (Absence of the assessed quality)
1-2-3 (Low)
4-5 (Moderate)
6-7 (High)
8-9-10 (Very high)

One of the reasons for the substitution of the plasma arc process is its high energy demand. Theoretically, the energy requirement to produce the first reaction to NO is ~0.9 kWh/KgNO but the plasma arc process consumed ~33 kWh/KgNO. Furthermore, the theoretical equilibrium value for NO at 3000°C is 6% as opposed to the 1.2% obtained in the commercial processes. New plasma processes being developed in the laboratory appear to have increased the yield of NO and reduce the energy requirements. Fauchais and Baronnet/13/ claim that plasma processes could be developed with energy requirements of the order of ~7 kWh/KgNO (comparable to the conventional process). Nevertheless, the increase in cost of the natural gas could make a plasma process competitive in 1985 in France. The potential market for the plasma production of NH_3 and HNO_3 is very large. But one of the factors which will decide the choice between a plasma process and the conventional one will be the relative costs of natural gas and electricity. A recent study by Estey and Connolly/17/ further confirms the above.

Plasma nitrogen fixation, as a research program, has a moderate potential because of the relatively high cost of the natural gas and hydrogen. In addition, its potential for joint research ventures is also limited. Its scoring value is far lower than the production of basic chemical feedstocks or methanol from coal.

5.4 Synthesis-Gas from Municipal Refuse

As urban populations grow, garbage disposal becomes increasingly complex and costly. Water, air and soil contamination as well as land requirements are major obstacles to waste disposal by dumping. InterGroup Consulting Economists Ltd/49/ have made a production of the growth in volume of municipal solid waste for the 163 larger municipalities in Canada from 1985 to 2025 (Table V). One of the conclusions of the report is that the refuse from the above municipalities have a total potential equivalent to 19 million barrels of oil annually. The project to produce fuels from municipal refuse is sound environmentally and energy efficency-wise.

Municipal refuse as a source of energy began to be developed in the early 1970's. However, the oscillations in the petroleum prices have put to rest many projects. Garbage utilization schemes, are very much in the limelight. But the project approach has changed from total resource-recovery (metals, glass, plastics, etc) to plain mass-burning of largely untouched refuse. Three cities in Los Angeles County have unveiled plans to build plants to obtain steam from municipal waste and CSI Resource Systems Inc, a Boston-based engineering firm, has revealed plans for 200 garbage-to-energy plants for the US.

TABLE V

Municipal Solid Wastes
Feedstock Supply Ranges: 1985-2025/49/

Region	Cities	1985		2005		2025	
		Cost ($/tonne)	Quantity 1/ (000 tonnes)	Cost ($/tonne)	Quantity 1/ (000 tonnes)	Cost ($/tonne)	Quantity 1/ (000 tonnes)
Central	Hamilton	7.19	195-232	14.88	214-380	15.74	234-619
	Montreal	7.19	1008-1201	14.88	1063-1906	15.74	1120-2926
	Ottawa-Hull	7.19	280-333	14.88	373-661	15.74	494-1306
	Quebec	7.19	213-253	14.88	1188-2106	15.74	1327-3512
	Toronto	7.19	1054-1255	14.88	1188-2106	15.74	1327-3512
Manitoba	Winnipeg	8.12	214-255	13.34	236-418	14.20	259-682
Alberta	Calgary	0	204-242	0	312-554	.25	469-1245
	Edmonton	0	230-273	0	324-574	.25	449-1192
West Coast	Vancouver	2.82	450-536	6.67	533-943	7.96	618-1635

Source: *InterGroup Consulting Economists Ltd.*

1/ Cellulosic tonnage at 35 percent moisture content; costs include processing and evaluation of opportunity values relative to coal; ranges of tonnage represent different assumptions about MSW generation rates and the proportion dedicated to materials recovery.

Note:
The MSW feedstock supply data were compiled with the end use of liquid fuel production in mind but it is evident that the feedstock could also be used in power production through combustion.

Technical evaluations show that by the end of the century, 50% of the US refuse will be burned instead of dumped in landfills. The prime motivation of such a policy is the increasing scarcity of landfill space, combined with the rising cost of trucking wastes to more-distant landfills.

The projects face a public concern: the emission of highly toxic pollutants. C.O. Velzy in a report for Argonne National Laboratory/50/ claims that in urban areas or regions with air pollution problems, "addition of acid-gas removal devices, along with ultra-high-efficiency (99% plus) particulate removal devices should be considered". J.L. Kuester, Professor of Chemical Engineering at Arizona State University, has analyzed the pyrolysis of municipal refuse. Some of the methods include the use of microwaves, incomplete combustion, indirect heating methods, etc. Although no process can be called trouble-free, Kuester considers that, "Pyrolysis development is of major importance with regard to producing synthesis gas appropriate for indirect processes that include a downstream conversion step".

A process developed in 1983 at the University of Manchester will transform municipal refuse into oil with a calorific value of 40 000 MJ/Ton/53/.

The use of plasma incinerators for the pyrolysis of municipal waste has had less coverage than the use of plasma to treat highly toxic waste/51,52/. Nevertheless, there are many and solid reasons, as explained above, to consider the production by plasma of synthesis-gas from the pyrolysis of municipal waste.

Ontario Hydro is presently a co-proponent of a proposal to develop a plasma process to pyrolyze municipal refuse. From a research point of view, a project of this kind requires instrumentation and ancillary equipment (to sort and shred the incoming refuse, and collect the solids) which could be of considerable complexity and cost and which OHRD lacks. However, political and economic considerations show that the project has a high potential for joint ventures. In addition, although figures are not available, synthesis-gas would have a large added value relative to municipal refuse. This makes the project comparable, in terms of research viability, to the production of methanol from coal.

5.5 Phosphorus and Phosphoric Acid

Phosphoric acid is one of the three major-volume mineral acids. Major end uses are fertilizers (85%), detergent materials (5%) and food processing (5%). It is produced either by reacting phosphate rock with sulfuric acid or burning elemental phosphorus and subsequent reaction with water.

Phosphorus, on the other hand, is obtained by reducing in electric furnaces phosphate rock with carbon (coke) and silica as acids. Detergent phosphate materials, mainly sodium tripolyphosphate, account for about half of the elemental phosphorus consumption down from about 60%, 15 years ago. Bans of phosphates in detergents is affecting negatively the demand of this product. The technologies of these products are very mature and hence, improvements in the processes' productivity will come from new technologies.

The application of plasma to the production of elemental phosphorus has received scanty attention in the past/54/. Goldberger and Baroch/57/ used a plasma jet to fluidize a bed of coke and silica to reduce phosphate rock. Another plasma process developed by Foex et al/58/ incorporates a sophisticated reactor design where a rotating furnace is heated by an arc between two plasma jets located at each end of the furnace. The feeding of the rock, silica, and coke takes place at the top and the phosphorus and molten slag is removed from the bottom of the furnace.

In a recent paper, Chase et al/59/ have shown that the continuous operation of a hot graphite plasma reactor, using methane as the phosphate rock reducing agent can yield up to 80% of phosphorus. The net power requirements were surprisingly large (24 kWh/lb of phosphorus) when compared to the theoretical value (7 kWh/lb of phosphorus). This difference was attributed to the large heat losses observed in bench scale experimental setups.

This project has, for the selection purposes, a series of drawbacks. These are: low sales volume compared to other programs, low added value to raw materials and energy costs and limited expertise and experimental feasibility in Ontario Hydro.

5.6 Cement Production

Cement manufacturing is the second most energy intensive industry in Ontario and tenth largest user of electricity/55/. This industry had a volume sales of $780 million for 1983 and ranks fourth by its added value.

ASTM specifications C 150-60 and C 175-61 define Portland cement as "the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates, to which no additions have been made subsequent to calcination other than water and/or untreated calcium sulfate, except that additions not to exceed 1% of other materials may be interground with the clinker at the option of the manufacturer...".

Cement manufacturing technology has not radically changed over the last few decades. The cement manufacturing process can be divided in three parts:

1) Processing of raw materials
2) Kiln operation
3) Cement mill operation

The last two steps consume 95% of the energy for the entire process. Also, the consumption of electricity in the cement industry is estimated to be 100 kWh/Tonne. No reduction in this figure is forecast. On the contrary, more requirements in the environmental field regarding different forms of pollution will undoubtedly lead to an increase in the consumption of electricity per tonne of cement.

The applications of high temperature plasmas to the cement industry has been proposed by Tylko/56/, Ettlinger et al/6/ and more recently by Drouet/3/.

Tylko developed a plasma reactor for the production of a wide range of hydraulic cements, including portland. Such a reactor can be installed into existing plants to provide excess thermal energy preventing contamination in the rotary kiln. Preliminary estimates indicate that cement could be 25% cheaper than that produced with conventional methods. Indeed, grinding energy requirements would be considerably lower. Also the replacement of the kiln by a plasma furnace could mean a 40% reduction in the capital costs/3/.

A comparative evaluation of this project research potential is shown in Table IV. Both its added value and its potential for flow sheet simplification are high. However, OHRD would require considerable investments in equipment and expertise to develop a research program based on the production of cement by a plasma reactor. Thus according to the scoring system presented in Table IV and Appendix 1, this project would rank sixth by its research potential.

6.0 CONCLUSIONS

Plasma technology is a $359 million industry in the US in 1984 and will rise to $10.5 billion by 1995. At the same time, industrial chemicals are by their added value, the second manufacturing sector, and rank third among the most energy intensive industries. Indeed, only pulp and paper and iron and steel mills consumed more electricity than the chemical industries.

Given the extraordinary potential that the chemical industry has to incorporate plasma technology, the lack of a more intensive research effort both in the public and private sectors is surprising. And, thus, two factors appear to act against further development of this technology: the complexity of plasmachemistry and plasma reactor engineering, and a certain degree of inertia or caution on the part of decision makers. In any event, the success of this technology depends on a number of variables in which electric power rates is but one of them.

A brief review of plasma fundamentals confirms that plasma reaction engineering is virtually unexplored and, indeed, many processes will be economically viable if areas such as high temperature catalysis and reactor design are developed. Ontario Hydro Research Division is currently evaluating the possibility of incorporating plasma technology into industrial chemical processes.

To select the most attractive research projects, a number of industrial chemical processes were chosen as part of a preliminary selection. The following factors were considered:

1) Sales volume
2) Added value ratio
3) Kind of raw materials and cost
4) Potential for simplifying the conventional process
5) Viability for the project to be carried out at OHRD
6) Potential for developing joint research programs with the public or private sector.

The initial selection of the above conventional processes was purely qualitative and resulted in the following six processes:

1) Production of basic petrochemical feedstocks from low grade coals.
2) Methanol from coal via synthesis-gas
3) Synthesis-gas from municipal refuse
4) Nitrogen fixation for fertilizers
5) Phosphorus and Phosphoric acid
6) Cement production

These six potential projects were ranked according to a semi-quantitative scoring method. Because of its high added value ratio, and sales volume, the production of basic petrochemicals from coal was the project with the highest score. This project has in addition three important features which further favoured its choice, namely its potential for cooperative projects, its experimental viability at OHRD and its potential to simplify the flow chart of the conventional process.

Based on the same considerations as above the other projects ranked as follows: Methanol from coal and synthesis-gas from municipal refuse had very similar scores; Nitrogen fixation; Cement production; and Phosphorus and H_3PO_4 production.

7.0 RECOMMENDATIONS

Based on the preliminary and final selection of the chemical processes reviewed in this report, the following recommendations are made:

1) A research program based on the production of basic petrochemical feedstocks from low grade coals should be designed and implemented.

2) Complementary with the previous program, it is recommended that a project on the production of methanol via synthesis-gas from low grade coals be developed.

3) The production of synthesis-gas from municipal refuse, might be as interesting as the previous project. Therefore, and given the fact that there is a research project underway in which OHRD is co-participant, it is recommended that OHRD seek access not only to the energy and environmental data but to all phases of the project regardless of our degree of participation in any of them.

ACKNOWLEDGEMENTS

The Scoring Method used in this report for the selection of the research programs owes part of its configuration to the following researchers: Profs. M. Boulos and E. Chornet of the Université de Sherbrooke, Prof. J. Corella of the Universidad de Zaragoza, Spain and Prof. W. Gauvin of McGill University, Montreal. To all of them my appreciation.

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APPENDIX I

1. Evaluation and Selection of the Research Program

Selecting an appropriate R&D decision methodology to support program management is to some degree a dynamic process in itself. A number of review papers on the methods for evaluating R&D projects has been published in the last 20 years/60-63/. Although, the number of evaluating methods described in the literature exceeds thirty, many of them are improvements of previous ones. Thus, a great majority of the methods are based on four fundamental ones. These are: economic; decision theory; constrained optimization; and scoring. A brief description of them follows.

2. Economic Methods

They are based on the capital budgeting techniques used in any study based on engineering economics. That is, concepts such as discounted cash flow, present worth, and interest rates of return. Capital budgeting techniques are very well defined, and procedures to put them in practice are well established. Economic methods are well suited for product oriented R&D and less so for research laboratories in the public sector. Their applicability is limited because: (1) reliable input data in dollars is hard to obtain, (2) they cannot be used to analyze projects at a number of funding levels. In that case more sophisticated methods are required.

A technique frequently used is that of the benefit cost ratio. In it, costs are the total resource costs of supporting the research and benefits are the net earnings to be realized from future product sales. The stream of project costs and benefits should be present valued using an appropriate discount rate. If the ratio benefits/costs < 1 the project is, generally cancelled. Benefit cost ratios can incorporate a wide number of considerations such as risk factors which diminish the project benefits. For instance, the technology transfer process might fail or even the market might reject the product.

The benefit cost ratio does not include non-economic considerations such as, social, environmental, and political costs or benefits of the research product. The inclusion of these factors in the method is, often, difficult since they are difficult to be expressed in the unit of measurement: dollars.

Advantages of the technique are that it requires from decision makers to clearly quantify their evaluation of the project. Also, the ratio has an obvious interpretation that makes project

rejection possible without unnecessary comparison with other projects.

The method has certain shortcomings such as: (1) the difficulty in expressing certain social or, in general, noneconomic events in dollars, (2) it does not recognize resource constraints, (3) it cannot reflect the level of risk facing the research project and (4) the, already mentioned, fact that economic methods are not useful for evaluating the consequences of alternative funding levels since each element of the benefits must be reassessed if the funding level is increased or reduced/62/.

3. Checklist and Profile Chart

This is the simplest form of project evaluation and involves the completion of a checklist or profile chart for each project considered.

Factors which are considered determinant for the outcome of the project are listed. Each project is then subjectively rated on the basis of each factor listed. The opinions of professionals expert in the project could be incorporated into the design of the profile chart and their opinions averaged.

Checklists have the advantage of simplicity and ease of use and at the same time provides a formal structure to the process of R&D decision making. Checklist factors are easily matched with information readily available. Indeed, certain types of information are nearly impossible to include in more quantitative methods. Also, particular weaknesses of individual projects are quickly identified by their poor ratings on certain criteria.

Although a checklist or profile chart is a useful and appealing tool to summarize and present available information on R&D, it can also be dangerous in that complex problems may be overlooked. For, even if many important factors may be included in a profile chart the relevance or importance of each individual factor is left indeterminate. In addition, it is difficult to know whether the respondents have given proper consideration to their answers.

4. Decision Trees Diagramming

When viable this method provides a more rigorous description of the R&D decision process and offers a much better basis for making decisions than other methods. Complex R&D projects can be displayed in a concise manner and the stochastic nature of their outcome is fully recognized. This method is well suited for a research program constituted by a number of projects and subprojects whose outcomes are interdependent.

Before a decision tree diagram can be implemented the following must be known:

1) Cost estimates for each projects or subprojects of the program.

2) An evaluation of the benefits resulting from the successful completion of the program, and

3) An estimation of the probability distribution for each project or subproject.

Obviously, better and more complete information will result in better R&D decisions. However, increased information requirements raise the cost of applying the method. Figures A-1 and A-2 illustrate the decision tree method for a research program which consists of project A and subproject B in sequence.

Project A has two alternatives: a high level of funding (cost = 5) and a low level (cost = 2). Four outcomes of research project A were adopted. For high-level funding were considered two outcomes: one with 80% chances of being highly successful and the other one with only 20% chances[2]. For a low-level funding were taken two possible outcomes with 40 and 60% chances of succeeding. Thus, the four possible outcomes led to the decision points 2, 3, 4 and 5. The two last ones will not be developed further for the decision points 2 or 3. The rest of Figure A-1 is self-explanatory except for the figures in the ellipses which are the estimated values of the product resulting from the different set of decisions taken at points 2 and 3.

The optimum decision path is obtained applying the algorithm

$$\mu = \left(\sum_{i=1}^{n} \rho_i \ \nu_i \right) - c$$

in which μ is the net of cost of following a path, c is the cost for a given decision, and ρ and ν are the probability density and value of outcome ith being successful.

For example, starting at the right-hand side of Figure A-1 the expected values

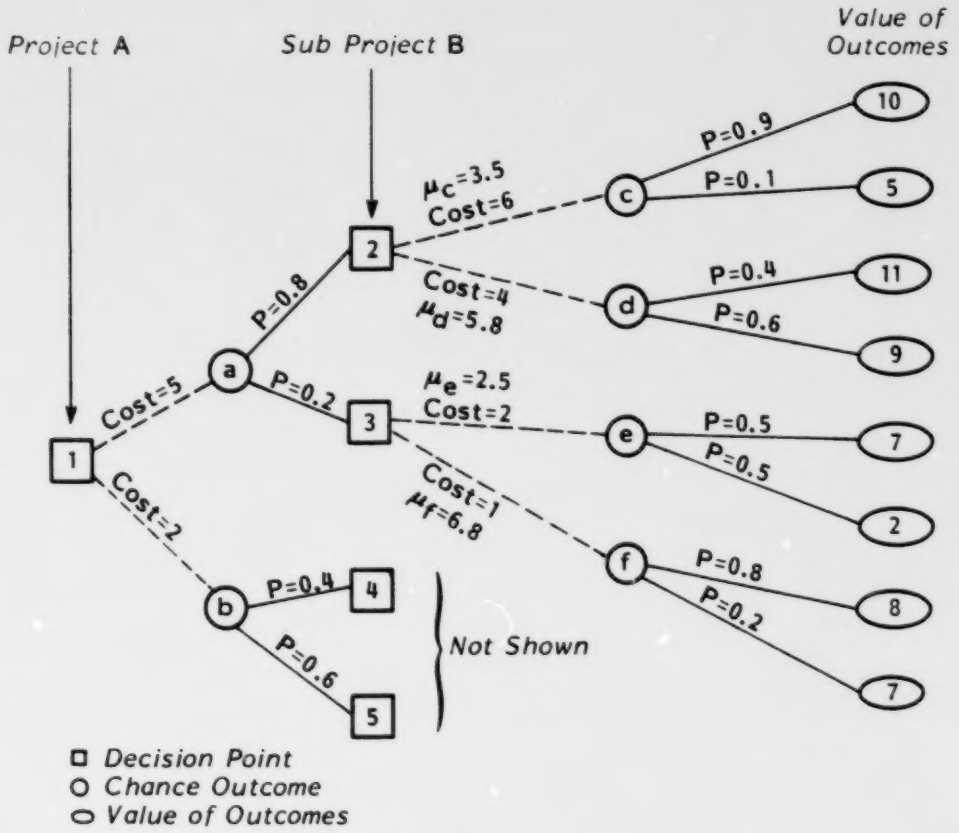

FIGURE A-1

DECISION TREE FOR RESEARCH PROGRAM

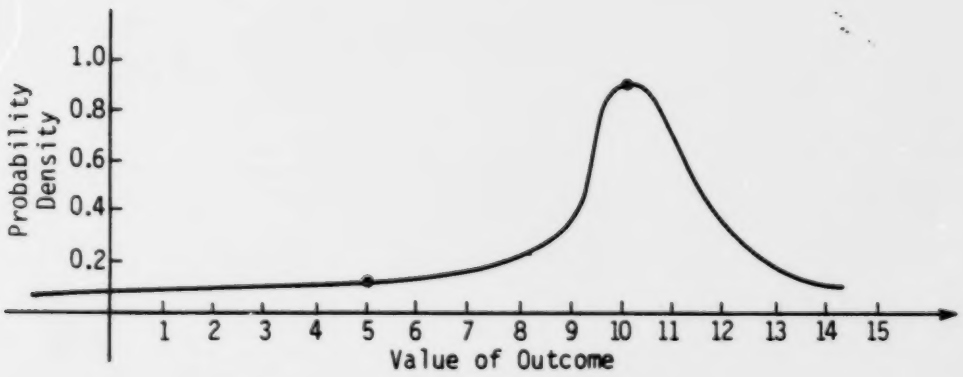

FIGURE A-2

PROBABILITY DISTRIBUTION OF OUTCOMES FOR SUBPROJECT B

$$\mu = \sum_{i=1}^{n} \rho_i \nu_i$$

at the points c and d are:

c: 10 x 0.9 + 5 x 0.1 = 9.5; μ_c = 9.5 - 6 = 3.5
d: 11 x 0.4 + 9 x 0.6 = 9.8; μ_d = 9.8 - 4 = 5.8

Thus, depending on the level of funding at decision point 2 subproject B will have 3.5 or 5.8 as net of cost.

The same calculations for chance points e and f yields 4 and 7.6 for the expected value, and μ_e = 2.5, μ_f = 6.8 for the net cost.

The next step is the selection of the branches with the highest net of cost at decision points 2 and 3, that is μ_d and μ_f, which now will play the role of values of the outcomes from "a" is:

a: 5.8 x 0.8 + 6.8 x 0.2 = 6; μ_a = 6 - 5 = 1

Therefore the net of cost of following the decision 1-a-2-d is 1 and has highest expected return. Before deciding the level of support for project A, one should follow the same procedure for the other branch from decision point 1.

One major drawback of the above analysis is that the outcomes at each chance point are represented as a few points (two in this case) rather than a continuous distribution of possible outcomes. For example, node "c" has two outcomes with a 90% aut 10% chances of happening. However, the rigorous way of representing the outcomes at "c" is by Figure A-2. It is clear now that two discreet values can hardly represent the probability distribution of outcomes for subproject B. In addition, a number of outcomes are negative and those may have an important influence in the decision to support project A. Adding more branches to the chance node would provide a better representation of the probability distribution but the complexity of the calculations involved in identifying an optimal decision path would increase rapidly. Replacing each of the chance points with a probability distribution produces a stochastic decision tree. Stochastic decision trees generally provide a more accurate description of the R&D decision process and offer a better basis for making decisions than other methods. Nevertheless, the improvements have, at times, a prohibitive price since the probability distribution of each

unknown research project must be estimated. Also, the cost estimates for each subproject must be calculated and the potential benefits of every outcome (successful completion of a program) must be assessed. Finally, stochastic decision tree analysis does not deal with resource constraints.

5. Scoring Methods

Scoring methods have been extensively used in R&D project selection/63,64/. As opposed to profile charts, in which individual criteria are not weighted, scoring models assigns weights to individual criteria and summarize the results as a single project score.

There are a number of methods for deriving criteria weights which range from simple rank ordering of criteria to various types of paired comparisons.

These are some of the advantages of the scoring methods.

1) They are the only methods specifically designed to incorporate non-economic criteria.

2) They use input data in the form of subjective estimates provided by knowledgeable people.

3) They use subjective "guesses" overtly where the other methods generally require more costly and complex methods.

4) Scoring methods produce results that are, on an average 90% rank-order consistent with economic and constrained methods based on linear and dynamic programming techniques.

Scoring methods are effective analytical tools when the data requirement and complexity of more "rigorous" approaches are not justified. The frequency of their use indicates the ease of implementation and their suitability to large, public sector, research centers. Aspects such as: uncertainty in the data, difficulties in the quantification of some factors and qualitative consideration can be better addressed by a scoring method.

These methods are, also, more suitable during basic research and exploratory development which is our case.

6. Application of the Scoring Method

First Step: Developing and listing of program elements.

This involves:

- Examination of the objectives of OH relative to the development of plasma technology.
- Assessment of the state of the art in the application of plasma technology to the chemical industry.
- Solicitation of ideas from other research centers, universities, and in general from the literature.

Second Step: Select and define the decision criteria.

Sales Volume	Among the economic criteria this is one of the most important ones, for it gives a direct indication of the probable demand of energy and social impact.
Ratio	The ratio of the added value to the total cost of materials plus utilities is an economic indicator of the relative added value.
Availability and Cost of Raw Materials	Imports and transportation costs should be minimized for the industrial process and the raw materials should be located preferably in Ontario.
Potential to Simplify Conventional Processes	The elimination of the pulverization, drying and separation processes should reduce both capital costs and energy costs.
OH Expertise and Experimental Feasibility	This criterion includes factors such as equipment available, instrumentation, and technical information available. It penalizes new requirements in expertise and equipment not presently available in OHRD.
Potential for Cooperative Projects	This criterion is an indicator of the possibility for joint research programs in the chosen area. Projects with a strong social incidence are more suitable for collaboration with the private sector. On the other hand, energy projects have a fertile area of co-operation in oil companies.

Energy Requirements	No reliable figures were available for most of the processes. Furthermore, the production of petrochemicals from coal has a large number of processes and variables which make, very uncertain, energy requirements.

Third Step: Weighting of the decision criteria.

It would involve the selection of a team of recognized experts in fields such as: gas and liquid fuels from coal and refuse, and in general energy processes. This panel should estimate the weighting to rank the selection criteria. For example the potential for establishing cooperative research programs has a different weight than, say, the volume sales of the process. In this study a group of researchers, experts in the Chemical Industries, as well as in plasma technology, were consulted. They quantified their views on the relative importance of each criterion for the selection of programs. They established the importance of those criteria by weighting them in the range 0 to 1. For example, a criterion very determinant in the selection success could be rated as 0.8, whereas, a criterion of secondary importance could be rated as 0.3. An average of these scores was made and appears in Table IV of the main text.

Fourth Step: Ranking of the projects.

This is established by comparing the scores of the projects which is given by the expression:

$$S_i \sum_{i=1}^{n} \sum_{j=1}^{m} C_{ij} W_{ij}$$

where C is the score given to project ith (we have selected 6 projects in this case) having a weight of W_{ij} for the decision criterion jth. In our particular case the score for the program was:

$$S_i = \sum_{i=1}^{6} \sum_{j=1}^{6} 10\, C_{ij} W_{ij} - R_{i3}$$ in which C_i is the criterion ith.

High cost or unavailability of raw materials, R_{i3} has a negative incidence in the successful outcome of the process hence its sign in the above expression.

Table IV displays the six projects with their corresponding scores. The rank is therefore:

1) Basic Petrochemical Feedstocks from Coal.

2) Methanol from coal and synthesis-gas from Municipal refuse.

3) Nitrogen Fixation

5) Phosphorus and Phosphoric Acid

4) Cement Production

Therefore, a long-term research program should be established for the production of Petrochemicals and Methanol from coal, and a medium-term program should be established for the production of synthesis-gas from municipal refuse.